

9.2 Volume Metering System Checks. Same as Method 5, Section 9.2.

#### 10.0 Calibration and Standardizations

NOTE: Maintain a laboratory log of all calibrations.

10.1 Sampling Equipment. Same as Method 13A, Section 10.1.

10.2 Fluoride Electrode. Prepare fluoride standardizing solutions by serial dilution of the 0.1 M fluoride standard solution. Pipet 10 ml of 0.1 M fluoride standard solution into a 100-ml volumetric flask, and make up to the mark with water for a  $10^{-2}$  M standard solution. Use 10 ml of  $10^{-2}$  M solution to make a  $10^{-3}$  M solution in the same manner. Repeat the dilution procedure, and make  $10^{-4}$  and  $10^{-5}$  M solutions.

10.2.1 Pipet 50 ml of each standard into a separate beaker. Add 50 ml of TISAB to each beaker. Place the electrode in the most dilute standard solution. When a steady millivolt reading is obtained, plot the value on the linear axis of semilog graph paper versus concentration on the log axis. Plot the nominal value for concentration of the standard on the log axis, (e.g., when 50 ml of  $10^{-2}$  M standard is diluted with 50 ml of TISAB, the concentration is still designated " $10^{-2}$  M").

10.2.2 Between measurements, soak the fluoride sensing electrode in water for 30 seconds, and then remove and blot dry. Analyze the standards going from dilute to concentrated standards. A straight-line calibration curve will be obtained, with nominal concentrations of  $10^{-4}$ ,  $10^{-3}$ ,  $10^{-2}$ ,  $10^{-1}$  fluoride molarity on the log axis plotted versus electrode potential (in mv) on the linear scale. Some electrodes may be slightly non-linear between  $10^{-5}$  and  $10^{-4}$  M. If this occurs, use additional standards between these two concentrations.

10.2.3 Calibrate the fluoride electrode daily, and check it hourly. Prepare fresh fluoride standardizing solutions daily ( $10^{-2}$  M or less). Store fluoride standardizing solutions in polyethylene or polypropylene containers.

NOTE: Certain specific ion meters have been designed specifically for fluoride electrode use and give a direct readout of fluoride ion concentration. These meters may be used in lieu of calibration curves for fluoride measurements over a narrow concentration ranges. Calibrate the meter according to the manufacturer's instructions.

#### 11.0 Analytical Procedures

11.1 Sample Loss Check, Sample Preparation, and Distillation. Same as Method 13A, Sections 11.1 through 11.3, except that the NOTE following Section 11.3.1 is not applicable.

11.2 Analysis.

11.2.1 Containers No. 1 and No. 2. Distill suitable aliquots from Containers No. 1 and

No. 2. Dilute the distillate in the volumetric flasks to exactly 250 ml with water, and mix thoroughly. Pipet a 25-ml aliquot from each of the distillate into separate beakers. Add an equal volume of TISAB, and mix. The sample should be at the same temperature as the calibration standards when measurements are made. If ambient laboratory temperature fluctuates more than  $\pm 2$  °C from the temperature at which the calibration standards were measured, condition samples and standards in a constant-temperature bath before measurement. Stir the sample with a magnetic stirrer during measurement to minimize electrode response time. If the stirrer generates enough heat to change solution temperature, place a piece of temperature insulating material, such as cork, between the stirrer and the beaker. Hold dilute samples (below  $10^{-4}$  M fluoride ion content) in polyethylene beakers during measurement.

11.2.2 Insert the fluoride and reference electrodes into the solution. When a steady millivolt reading is obtained, record it. This may take several minutes. Determine concentration from the calibration curve. Between electrode measurements, rinse the electrode with water.

11.2.3 Container No. 3 (Silica Gel). Same as in Method 13A, Section 11.4.2.

#### 12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 Nomenclature. Same as Method 13A, Section 12.1, with the addition of the following:

M =  $F^{-}$  concentration from calibration curve, molarity.

12.2 Average DGM Temperature and Average Orifice Pressure Drop, Dry Gas Volume, Volume of Water Vapor and Moisture Content, Fluoride Concentration in Stack Gas, and Isokinetic Variation. Same as Method 13A, Sections 12.2 to 12.4, 12.6, and 12.7, respectively.

12.3 Total Fluoride in Sample. Calculate the amount of  $F^{-}$  in the sample using Equation 13B-1:

$$F_t = \frac{KV_t V_d M}{A_t} \quad \text{Eq. 13B-1}$$

Where:

K = 19 [(mg-l)/(mole-ml)] (metric units)  
= 0.292 [(gr-l)/(mole-ml)] (English units)

#### 13.0 Method Performance

The following estimates are based on a collaborative test done at a primary aluminum smelter. In the test, six laboratories each sampled the stack simultaneously using two sampling trains for a total of 12 samples per

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sampling run. Fluoride concentrations encountered during the test ranged from 0.1 to 1.4 mg F<sup>-</sup>/m<sup>3</sup>.

13.1 Precision. The intra-laboratory and inter-laboratory standard deviations, which include sampling and analysis errors, are 0.037 mg F<sup>-</sup>/m<sup>3</sup> with 60 degrees of freedom and 0.056 mg F<sup>-</sup>/m<sup>3</sup> with five degrees of freedom, respectively.

13.2 Bias. The collaborative test did not find any bias in the analytical method.

13.3 Range. The range of this method is 0.02 to 2,000 µg F<sup>-</sup>/ml; however, measurements of less than 0.1 µg F<sup>-</sup>/ml require extra care.

### 14.0 Pollution Prevention. [Reserved]

### 15.0 Waste Management. [Reserved]

### 16.0 Alternative Procedures

16.1 Compliance with ASTM D 3270-73T, 91, 95 "Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Semiautomated Method)" is an acceptable alternative for the distillation and analysis requirements specified in Sections 11.1 and 11.2 when applied to suitable aliquots of Containers 1 and 2 samples.

Analyte	CAS No.	Sensitivity
Total fluorides as Fluorine .....	7782-41-4	Not determined.

1.2 Applicability. This method is applicable for the determination of fluoride emissions from roof monitors at primary aluminum reduction plant potroom groups.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

### 2.0 Summary of Method

2.1 Gaseous and particulate fluoride roof monitor emissions are drawn into a permanent sampling manifold through several large nozzles. The sample is transported from the sampling manifold to ground level through a duct. The fluoride content of the gas in the duct is determined using either Method 13A or Method 13B. Effluent velocity and volumetric flow rate are determined using anemometers located in the roof monitor.

### 3.0 Definitions

*Potroom* means a building unit which houses a group of electrolytic cells in which aluminum is produced.

*Potroom group* means an uncontrolled potroom, a potroom which is controlled indi-

### 17.0 References

Same as Method 13A, Section 16.0, References 1 and 2, with the following addition:

1. MacLeod, Kathryn E., and Howard L. Crist. Comparison of the SPADNS-Zirconium Lake and Specific Ion Electrode Methods of Fluoride Determination in Stack Emission Samples. *Analytical Chemistry*. 45:1272-1273. 1973.

### 18.0 Tables, Diagrams, Flowcharts, and Validation Data. [Reserved]

### METHOD 14—DETERMINATION OF FLUORIDE EMISSIONS FROM POTROOM ROOF MONITORS FOR PRIMARY ALUMINUM PLANTS

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 13A, and Method 13B.

### 1.0 Scope and Application

#### 1.1 Analytes.

vidually, or a group of potrooms or potroom segments ducted to a common control system.

*Roof monitor* means that portion of the roof of a potroom where gases not captured at the cell exit from the potroom.

### 4.0 Interferences

Same as Section 4.0 of either Method 13A or Method 13B, with the addition of the following:

4.1 Magnetic Field Effects. Anemometer readings can be affected by potroom magnetic field effects. Section 6.1 provides for minimization of this interference through proper shielding or encasement of anemometer components.

### 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.